UV absorption spectroscopy in optically dense fireballs using achromatic frequency doubling of a broadband modeless dye laser

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Optical diagnostics of fireballs, such as in high explosives and metal dust cloud combustion, are typically done in emission due to the intense luminosity, but because of the optical thickness of the fireball, the emission measurement is typically only representative of information near the surface of the fireball. Absorption techniques provide a path averaged measurement and give information about the inside of the fireball. Intense pulsed laser sources can penetrate an optically dense medium and still transmit enough light to disperse into a well-resolved spectrum, from which concentration and temperature information is extracted. In this study, the technique is extended to the UV spectral region by using a broadband frequency doubling technique. The output of a Nd:YAG(355 nm) pumped modeless dye laser can be spectrally dispersed using prisms and focused onto a type-I BBO crystal so that the angular dispersion of the light matches the external phase matching angle of the crystal for each wavelength in the laser. The generated dispersed UV light is recombined by another set of dispersive elements to generate a collimated beam of broadband UV light for the absorption measurement. The system is demonstrated using NO absorption in an electric discharge in the vicinity of 226 nm.

1. Introduction

Combustion measurements within the fireballs generated by explosives have several diagnostic hurdles owing to the multiphase dynamics, the high temperatures, short time scales, and high optical depths of the combustion event. Explosives are often enhanced by the addition of solid phase fuels which creates high temperature environments of particulate and gas phases within the fireball. The relevant diagnostic time scales within explosives systems is typically on the order of several microseconds necessitating diagnostics which can be performed in a single shot.

One of the key diagnostic capabilities is the characterization of temperatures within the fireball and the ability to monitor chemical species that evolve during the combustion. Optical techniques are more robust within the high temperature, multiphase environments where mechanical probes methods are difficult due to temperature limitations and slow response time. In fireballs containing reactive particles, it is possible that the temperatures of the solid phase and gas phase may be different due to kinetically limited and diffusion limited particle reactions. Spectroscopic diagnostics may be able to analyze the possible separation of particle and gas temperatures by examining the gas phase components of the flame thereby demonstrating the regimes of particle combustion.

The high luminosities of fireballs of energetic materials lend to the prevalence of emission based diagnostics. The condensed phase temperature can be determined by using optical pyrometry or by fitting the continuum from the condensed phase to a Planck distribution and has been used as a temperature diagnostic in energetic materials in many studies (Goroshin, Frost et al. 2006, Lynch, Krier et al. 2010). There is also precedent for using metal salt tracers to introduce vaporized atomic species into the combustion system to determine electronic excitation temperatures which can be extended to diagnostics of explosives (Gaydon 1974). Lewis et al. have shown that using atomic tracer elements seeded into explosives that a gas phase temperature can be measured from the relative intensities of the resulting atomic lines in the emission spectrum of the fireball (Lewis and Rumchik 2009). Emission from the diatomic species present in
the combustion of energetic materials (e.g. AlO) can also be fit to theoretical transitions to determine temperatures and concentrations (Peuker, Lynch et al. 2013).

In emission measurements, it has been shown that in both electronic transitions of single atomic species and in the measurements from diatomic species that the measurement may be subject to over-excitation (Gaydon 1974). In general, an emission temperature should be checked for rotational/vibrational equilibrium or by comparing to an absorption measurement. Another disadvantage of emission measurements is that species often do not have very many transitions available to be measured in combustion environments owing to the small number of low lying excited states. In the particular case of optically thick fireballs, it has been shown that the detonation products of gram scale and higher experiments that the attenuation lengths are on the order of a few centimeters implying that the temperatures derived from the emission measurements are typically only representative of the outer edge of the fireball (Peuker, Lynch et al. 2009).

The preferred measurement, in these cases, would be to probe the ground state in absorption, which not only allows access to more transitions, but is also able to probe information inside the fireball. However, absorption measurements in fireballs are difficult owing to the intense luminosity of the fireball and the high intensity and coherence required from a broadband source to penetrate the fireball to do the measurement. Experiments by Lewis et. al in fireballs of RDX attempted to probe the inside of the fireball revealing no significant difference between the apparent temperatures measured by emission spectroscopy of the interior of a RDX fireball and the outer edge after significant mixing (Lewis, Rumchik et al. 2013). Carney et al. demonstrated absorption in the NIR using a booster optical amplifier to measure the absorption of water vapor in the infrared to obtain a line-of-sight temperature measurement (Carney, Lightstone et al. 2011).

In previous work, Glumac was able to show proof-of-concept experiments using a modeless dye laser as a spectral source to do absorption spectroscopy measurements in optically thick fireballs (Glumac 2009). Modeless dye lasers offer a widely tunable, relatively high bandwidth (~1-10 nm) coherent source and have moderate divergence and high power. In optically thick regions, there is difficulty in passing sufficient signal to detector from other broadband sources due to the scattering of the light. The dye laser offers an intense, directional beam allowing the strong rejection of the fireball luminosity and sufficient signal at the detector even at 98% attenuation.

Dye beam wavelengths are limited to the near ultraviolet (UV) due to the nature of the available dyes. A great number of important diatomic and atomic transitions occur below these wavelengths necessitating broadband spectral UV sources that can access the transitions. The advantage of dye lasers is almost any wavelength can be reached by the appropriate selection of dye. This study utilizes broadband second harmonic generation (SHG) of the dye laser beam absorption measurements in several more atomic and diatomic species (e.g. NO, OH, CN, CH, AlF). The spectrum obtained from the NO \( \Lambda^2 \Sigma^+ \leftarrow X^2 \Pi \) band is compared to the simulation of the band using LIFBASE (Luque and Crosley 1999).

2. Methods

Dye laser configuration

The schematic of the entire setup is shown in Figure 1. A frequency tripled compact Nd:YAG laser (Quantel Brilliant) with 355 nm, 5 ns pulses at 20 Hz is used as the pump for the dye laser. The maximum power available from the laser is approximately 60 mJ per pulse. The built in flash-lamp/Q-switch delay on the laser is used to adjust the power to pump the dye with a minimum required power of about 4 - 10 mJ per pulse depending on the dye.

The dye laser configuration is demonstrated in previous work by Glumac to produce a modeless beam with about 5% efficiency (Glumac 2009). The 355 nm Nd:YAG beam is passed through a cylindrical lens to produce a horizontally spread beam and then focused down in the vertical direction by a second cylindrical lens onto a quartz dye cuvette 40 mm in length. The cuvette is tilted at a 20 degree angle to minimize etaloning effects. A full reflecting mirror is placed at one end of the laser cavity approximately 10 cm from the cuvette, though for a modeless laser this distance may vary without much consequence. The laser has no output coupler, and the front end is empty aside from an iris to prevent stray light and an achromatic collimating lens with a focal length of 175 mm to counteract the moderate divergence of the beam.

In cases where higher power and better beam shape is desired, Glumac shows that a partially reflecting mirror may be used at the front end of the cavity as long as the cavity is designed with very low finesse (Glumac 2009). Other work using modeless dye lasers for broadband CARS passes the initial dye beam through an amplifier to change the beam shape and divergence (Hahn, Park et al. 1997). The power of the pump beam may be increased by using a flowing dye cell since stationary dyes tend to degrade quickly under high pump powers. The power of the dye beam produced by
an empty cavity front end and a stationary dye cell is found to be sufficient for the systems examined in this work with about 5% efficiency.

**Figure 1. Schematic of the entire setup for a single shot absorption measurement.**

*Second harmonic generation*

The wavelengths produced by dye lasers are limited to wavelengths above 330 nm for Nd:YAG pumped dyes. To extend deeper into UV spectrum to access a much greater number of species, the beam can be passed through a non-linear crystal for SHG. Critical phase matching to the non-linear crystal allows for efficient SHG of a monochromatic beam by simply rotating the crystal to the optimum angle determined by the crystal cut. Wavelengths in a broadband beam which are outside the phase-matching bandwidth determined by the thickness of the crystal and the diameter of the beam incident on the crystal will typically have very low SHG efficiencies. The BBO-type I 7mm crystal with a cut angle of 52 degrees (Radiant Dyes) used in this study theoretically has only around 0.1 degree angular width of phase matching at the desired wavelengths. Shorter crystals will increase this angular acceptance provided higher spectral bandwidth at the expense of conversion efficiency.

The broadband nature of ultra-short laser pulses has led to the development of several techniques for increasing the phase matching bandwidth in crystals using the chromatic dispersion of the fundamental beam (Saikan 1976, Saikan, Ouw et al. 1979, Szabó and Bor 1990, Cheville, Reiten et al. 1992, Richman, Bisson et al. 1997, Richman, Bisson et al. 1998). The beam is spectrally separated by a dispersion element and then focused onto the crystal so that the critical phase matching condition is met for each wavelength without having to rotate the crystal. The dispersed second harmonic is then re-collimated and recombined using a second dispersive element to counteract the spectral separation. Several optimum configurations can be calculated iteratively for stock optics. A schematic of a possible dispersive system to obtain broadband SHG is shown in Figure 2. One possible configuration for achromatic phase matching in the region of 448-500 nm was determined by using a N-SF11 dispersion prism with a 60 degree apex angle and a 50 mm focusing lens set a distance 300 mm from the prism. The calculated incidence angles deviate less than 0.1 degree from the external phase matching angles of the BBO crystal. A second set of UV optics compensating for the dispersion can be used to re-collimate the beam.
Figure 2. Schematic of achromatic phase matching and beam re-collimation using a prism lens system.

Unlike the >100 nm bandwidth of ultra-short pulses, the bandwidth of the second harmonic pulse required for absorption spectroscopy of diatomic species is only a few nanometers in wavelength since the bandwidth of the fundamental beam is only about 10 nm and the dispersion of the spectrometer must be relatively high to analyze diatomic transitions.

Without spectral dispersion, the fundamental dye beam in this experiment was focused with a 50 mm focal length achromatic lens onto the BBO crystal so that the focus of the beam was slightly beyond the crystal to avoid damaging the crystal. The beam was then re-collimated using a UV fused silica (UVFS) 25 mm focal length plano-concave lens. It is found in previous studies that broadband light focused onto the crystal emerges nearly collimated in the horizontal direction, though the beam may be slightly spectrally dispersed (Saikan, Ouw et al. 1979). The re-collimating lens allows the collimation of the beam in the vertical direction but causes divergence in the horizontal direction necessitating cylindrical correction optics to shape the beam in the horizontal direction. The combined fundamental and second harmonic are first passed through a UVFS dispersion prism with an apex angle of 60 degrees to separate the fundamental from the second harmonic and then shaped with a UVFS cylindrical inverse telescope consisting of a 70 mm and 20 mm focal length UVFS plano-convex cylindrical lens. The resulting beam is approximately 2 mm in diameter as seen on a UV viewing card.

The UV beam is focused onto the 50 um slit of a 1260 mm focal length Czerny-Turner SPEX 1250 spectrometer with deviation angle of 11 degrees and a 3600 grooves/mm UV holographic grating. The detector is a GARRY 3000 which is a CCD line array of 3000 pixels each 7 um wide. The resolution achieved by this spectrometer is approximately 0.01 nm full width half maximum (FWHM) over a range of about 4 nm on the detector. Even at low dye beam powers, the generated SHG UV beam is sufficient to saturate the detector of the spectrometer.

Figure 3. (left) Modeless dye beam produced by Coumarin 460. (right) the SHG with only using a strong focusing condition on the crystal.
**NO measurement**

In order to examine the NO \( \text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi \) band with peak absorption around 226.3 nm as a test case for this technique, the fundamental dye beam was created by pumping a solution of Coumarin 460 (Exciton) in ethanol at 0.005 mol/L. The resulting bandwidth of the UV beam generated from the strong focusing of the dye beam onto the crystal was approximately 1 nm at full width at half maximum (FWHM) as shown in Figure 3 using an Ocean Optics USB2000 spectrometer to measure the bandwidth of the fundamental beam and the SPEX 1250 for the second harmonic. The spectral position on the detector was calibrated using a Ni hollow cathode lamp and checked against the position of the strong NO transitions.

At room temperature (~300 K) the NO \( \text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi \) transition has a strong absorbing band from 225-227 nm. The use of spectral dispersion of the broadband dye beam in order to obtain broadband SHG was not needed to resolve the structure of the NO \( \text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi \) transition over a one nanometer bandwidth from 226-227 nm. Instead, a strong focusing condition on the nonlinear crystal provided sufficient bandwidth to use as a continuum source to resolve the spectral structure of the NO in this wavelength region.

A test system of NO is generated in a sealed chamber using an electric arc discharge in air. The electrodes are mounted within a 5 cm wide sealed chamber with quartz windows. The amount of NO produced in the chamber is proportional to the duration of the arc. The absorption features were monitored on the raw spectrum during the arc discharge and provided a relative measure of the NO concentration.

3. Results and Discussion

An experimental measurement of an explosive fireball system is simulated by a single pulse measurement. The power pumping the dye laser is lowered to prevent detector saturation. The detector is set to a one second integration time and a reference pulse is taken by passing it through the empty chamber. An arc is then produced in the chamber for 30 seconds until the absorption signal is visibly noticeable over the noise from the laser and a second pulse is recorded. The absorbance from the single pulse measurement is shown in Figure 4. A simulation of NO absorption spectrum is produced by LIFBASE for comparison using the resolution of 0.1 nm obtained by spectrometer calibration and set to room temperature at 300 K.

![Figure 4. Single laser pulse measurement of NO compared to an optically thin spectrum simulated by LIFBASE for T=300K.](image)
The single pulse absorption measurement produces a high signal to noise spectrum across a 1 nm region with approximately 30 well resolved rotational lines. Such a spectrum can be fit to a temperature with high degree of accuracy. A comparison with an optically thin LIFBASE spectrum shows clearly the effects of optical depth in the spectrum, which enhance weaker lines at the expense of stronger ones.

At lower concentrations and optically thin conditions, obtaining a high quality single shot spectrum is more challenging. In a second series of tests, laser noise is reduced by increasing pump power and using a UVFS diffuser before focusing the light onto the slit of the spectrometer, however signal strength is also reduced. The laser is set to pulse continuously (20 Hz), and integration time is set to one second on the detector in order to obtain an averaged spectrum over the 20 pulses. A reference spectrum is taken in the empty chamber. The chamber is then filled with NO by producing an arc for five seconds or until only a slight absorption feature is qualitatively observed in the raw spectrum to produce an optically thin measurement. The resulting spectrum and comparison to the LIFBASE simulation is shown in Figure 5. Good agreement is shown between the simulation and resulting averaged spectrum from several laser shots and by lowering the concentration of NO.

![Figure 5. NO spectrum at low concentration from continuously pulsed laser (20Hz) integrated over 1 second compared to spectrum simulated by LIFBASE at T=300K.](image)

4. Conclusions

The use of dye lasers as a spectral source for an absorption measurement is shown to be able to extend into the UV beyond the limitations of pumped dye beams by using SHG. Measurements of the NO $A^2\Sigma^+ \leftrightarrow X^2\Pi$ absorption spectrum from 226-227 nm are demonstrated using a single pulse with well defined structure and good correlation to simulated spectrum at is shown for an average measurement over several pulses. Improved performance is expected by reducing noise from the laser and by splitting the pulse to perform a single shot experiment with simultaneous reference signal. Simulations that include optical thickness will also be necessary to obtain good temperature correlation with data.

Although a strong focusing condition of the dye beam onto the crystal produces approximately 1 nm of bandwidth for a measurement, bandwidth can be increased by using broadband phase matching techniques reviewed in this paper. This diagnostic provides a simple tool for obtaining a path averaged measurement and overcoming the difficulties of absorption spectroscopy in explosive fireballs and other optically thick combustion systems as shown in previous studies using the visible spectrum of dyes (Glumac 2009). Several atomic and diatomic species can be accessed for measurement by careful selection of dyes and crystal configurations.
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References


